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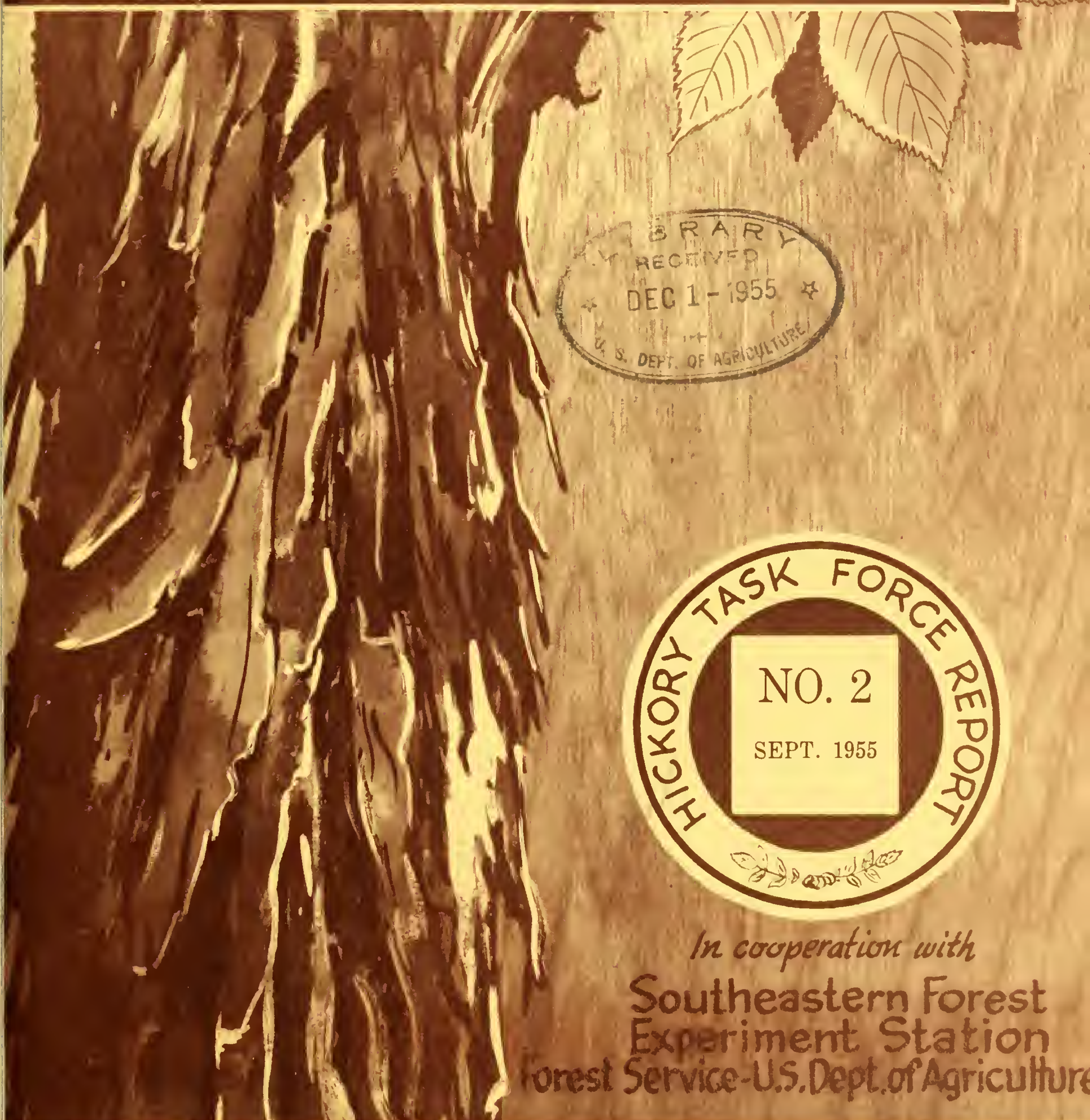
Chemistry of Hickory

by

Raymond L. Mitchell



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HICKORY TASK FORCE REPORT

NO. 2

SEPT. 1955

In cooperation with

Southeastern Forest Experiment Station
Forest Service-U.S. Dept. of Agriculture

FOREWORD

Hickory (Carya spp.) has earned the reputation of being one of the world's toughest woods. In shock resistance it has no equal. The reputation earned by hickory is based on the performance of high quality material in products requiring a high degree of strength and toughness.

Today, a limited quantity of high-grade hickory is available and its value and scarcity are well recognized by the wood-using industries. There is, however, a large volume of low-grade hickory that was bypassed when loggers cut our hardwood forests, and many land managers are troubled by the increasing amount of growing space occupied by it. Although this low-grade hickory does not possess the quality or properties required in many products, it is a potentially valuable wood for many uses.

A conference of federal, state, university, and industrial representatives was held in Clemson, S. C., in April 1953, and the Hickory Task Force was organized to promote the utilization of hickory. Accomplishment of this objective will be reached through research and publication of known information.

The Southeastern Forest Experiment Station has assumed the responsibility to edit, publish, and distribute reports containing information which will be developed under this program.

Full acknowledgment is due the many cooperating agencies and individuals who are making the project possible. Subject Matter Committee Chairmen are:

John Drow, Forest Products Laboratory, Madison, Wis., Growth and Properties of Hickory.
Roger Anderson, Duke University, Durham, N. C., Enemies of Hickory.
Roy M. Carter, N. C. State College, Raleigh, N. C., Manufacturing and Seasoning of Hickory.
John W. Lehman, Tennessee Valley Authority, Norris, Tenn., Products from Hickory.
Lenthall Wyman, N. C. State College, Raleigh, N. C., Hickory for Fuel.
C. E. Libby, N. C. State College, Raleigh, N. C., Hickory for Fiber.
Monie S. Hudson, Spartanburg, S. C., Treating Hickory.
Richard D. Lane, Central States Forest Experiment Station, Carbondale, Ill., Marketing of Hickory.

Walton R. Smith, Chairman
Hickory Task Force

See the inside back cover for a list of hickory reports planned.

CHEMISTRY OF HICKORY

By

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SUMMARY

Existing analytical data presented for several hickory and pecan hickory species are comparable to those of other hardwoods. Hickory therefore can be assumed to have a potential equivalent to that of other hardwoods as a source of chemical products from waste wood, whether on the basis of the whole wood or of the sugars obtained by hydrolysis. Some data on the composition of bark, nuts, and leaves are presented. Potential methods for chemical utilization of waste hickory wood, based on the carbohydrate fraction, are discussed.

INTRODUCTION

The limited amount of information available on the chemistry of hickory is probably due to the fact that this wood has been considered primarily for the manufacture of lumber products rather than as a potential raw material for chemicals. This report was prepared at the U. S. Forest Products Laboratory to summarize available information on the chemical composition of true hickories and pecan hickories for use by anyone interested in their chemical utilization.

COMPOSITION OF HICKORY WOOD

Ultimate Analysis

The elements composing the organic portion of wood are carbon, hydrogen, oxygen, and nitrogen. Wood also contains a small amount of ash that consists of very small quantities of various metallic and nonmetallic elements. The ultimate analysis--that is, the amount of the separate elements--has not been reported for hickory, but the composition would not be expected to differ from that of the species

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

shown in table 1. Wood contains approximately 50 percent of carbon, 6 percent of hydrogen, 44 percent of oxygen, and less than 1 percent of nitrogen and ash. Ultimate analysis of many species shows no distinction between hardwoods and softwoods, or between sapwood and heartwood.

Proximate Analysis

Proximate analysis is a more intensive form of chemical analysis in which the constituent compounds of a complex mixture are determined. The sum of the analytical components of wood exceeds 100 percent because some of the constituents, at least in part, are determined more than once; for example, pentosans are determined separately but also make up part of the holocellulose fraction. Analytical values for several species of hickory are recorded in table 2.

Extractives

Extractives form no part of the wood structure and may be removed by neutral solvents, such as water, alcohol, ether, alcohol-benzene, and acetone. They are largely responsible for the color, odor, taste, decay resistance, and corrosive properties of wood.

The extractives of hickory species have not been identified. Water-soluble extractives usually include tannins, sugars, polysaccharides of low molecular weight, coloring matter, and salts. The amount of water-soluble material obtainable from hickory is comparable to that from oaks. Tannin is absent or present in only small amounts in the water extract of several species of hickory wood that have been tested (table 3).

Ether-soluble extractives include oils, fats, fatty acids, resins, resin acids, phytosterol, and waxes. These materials, as well as a part of the tannins, are also soluble in alcohol-benzene. The small amount of ether-soluble material in hickory species so far analyzed is characteristic of hardwoods.

Ash

Ash makes up from 0.4 to 1.0 percent of the wood of the species analyzed. A wide variation of ash content may occur within a species; the minimum and maximum for shagbark hickory wood, for example, are 0.3 and 1.1 percent, respectively. [2/]

The chemical elements in wood ash, expressed as the oxides, are shown in table 4. These include potassium, phosphorus, and calcium, which are important fertilizer materials. Wood ashes cannot compete as a commercial fertilizer material except perhaps for local use.

Lignin

Lignin is the noncarbohydrate material that serves as a binder of the fibers and other structural elements, thus producing stiffness in wood.

2/ Bateman, E. Wood ashes and production of potash. Chem. and Metallurgical Eng. 21 No. 12: 615-619. 1919.

The percentage of carbon in lignin is greater than that of wood or cellulose and the major part of the methoxyl in wood is combined with lignin. Other chemical characteristics of lignin are its phenolic character, solubility in alkali, and insolubility in mineral acids. Lignin is readily attacked by most oxidizing agents.

The lignin content of the species of hickory analyzed so far is comparable to that found for other hardwoods, such as the oaks.

Holocellulose

Holocellulose is the fibrous, lignin-free fraction of wood. It includes alpha-cellulose and hemicullulose.[3/] Cross and Bevan cellulose consists of the alpha-cellulose and part of the hemicellulose. Pentosans, the major portion of the hemicellulose fraction, are the source of furfural. Holocellulose contains the acetyl groups that are the source of acetic acid in the wood. Hickory contains less acetyl than many of the other hardwoods.

Composition of Bark

The tannin in the bark of several hickory species has been determined (table 3). A tannin content of at least 8 percent is usually considered necessary for profitable commercial extraction.

Analytical data on the composition of pecan bark and other barks are given in table 5. The composition of bark differs from that of wood, in that bark has greater amounts of ash, extractives, "lignin," and smaller amounts of reducing sugar produced by hydrolysis with 72 percent sulfuric acid.

No general processes have been developed for the utilization of large amounts of bark, except as a fuel.

Composition of Nuts

The composition of the edible portion of pecan and hickory nuts is shown in table 6. The composition of pecan shells is compared with that of other nut shells in table 7. Pecan shells yield 12 percent of crystalline d-xylose by acid hydrolysis.[4/] Pecan shells contain 23.7 percent of tannin (condensed type) that produces a color on hide between that produced by sumac and hemlock.[5/]

Composition of Leaves

In studies in South Carolina, Metz found that hickory leaves contain more nitrogen and calcium than those of yellow-poplar, red maple, or American sweetgum (table 8). Yellow-poplar leaves contained slightly more magnesium than those

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3/ Ritter, G. J. and Kurth, E. F. Holocellulose, total carbohydrate fraction of extractive-free maple wood, its isolation and properties. Ind. and Eng. Chem. 25: 1250-1253. 1933.

4/ Thor, C. J. B. and Smith, C. L. Pecan shells as a source of d-xylose. Jour. Amer. Chem. Soc. 56: 1640. 1934.

5/ O'Flaherty, F. Tannin content of pecan shells. Jour. Amer. Leather Chem. Assoc. 36: 323. 1941.

of hickory. On a basis of these determinations and annual leaf fall, he found that hardwood stands return more nitrogen, calcium, and magnesium to the soil than do pine stands. Hickory was a leading contributor of these elements.

Chemical Utilization

Hickory is one of the neglected species as far as chemical utilization is concerned. There has been no chemical utilization of hickory except possibly by the destructive distillation industry to produce charcoal and volatile chemical products. The synthetic organic chemical industry has made uneconomic the production of methyl alcohol and acetic acid from wood. Distillation products are obtained in comparable yields from various hardwoods. They are derived from the extractives, lignin, cellulose, and hemicellulose in the wood (table 9).

Although the flavor of the decomposition products is thought to account for the preferred use of hickory in the smoking of meat, it cannot be attributed to any known difference in chemical composition between hickory and other hardwoods.

A possible use of waste hickory wood may be found in the production of sugars or sugar derivatives obtained by hydrolysis of the cellulosic fraction of the wood. The yields of potential and fermentable sugars from typical woods by laboratory methods are given in table 10.

The hexosans by similar methods may be converted to hydroxymethyl furfural, together with levulinic and formic acid. These materials may find an important place in the future of plastics, adhesives, solvents, and other industrial organic chemicals.

The carbohydrates of wood can be used to produce simple sugars (table 10). These sugars can be used as animal feeds, or can be converted by biological methods into a variety of organic chemicals or feed yeast.

Lignin, amounting to nearly a quarter of the wood, is of little economic importance at the present time. Potentially, it is a source of chemicals, and it might be used in plastics. The fundamental chemistry of lignin is being studied at the Forest Products Laboratory and at other laboratories throughout the world.

Plans for the chemical utilization of wood must take into account the entire wood substance. The production of such things as molasses, furfural, or levulinic acid appears unattractive when they are considered separately.

The chemical utilization of wood residues does have attractive possibilities, however, if properly integrated with forestry, logging, and sawmill operation.

Table 1.--Ultimate analysis of woods [1/]

Species	Elemental composition				
	Carbon	Hydrogen	Nitrogen	Oxygen	Ash
	Percent				
Larch, 103 years old					
Sapwood	49.57	5.85	0.17	44.19	.22
Heartwood	49.86	5.91	.12	43.99	.12
Pine, 104 years old					
Sapwood	50.18	6.08	.17	43.38	.19
Heartwood	54.38	6.31	.56	39.00	.15
Spruce, 75 years old					
Sapwood	50.03	6.05	.19	43.47	.26
Heartwood	49.55	6.18	.18	43.89	.20
Oak, 125 years old					
Sapwood	49.15	5.84	.35	44.24	.42
Heartwood	50.28	5.62	.28	43.66	.16
Beech, 180 years old					
Sapwood	48.92	5.86	.24	44.51	.47
Heartwood	49.06	5.91	.22	44.41	.40

1/ Schorger, A. W. The chemistry of wood and cellulose. 596 pp., illus. New York. 1926.

Table 2.--Data from proximate chemical analysis of hickory [1] [2] [3] (based on weight of ovendry wood)

Species	Material soluble in: [4]					Ash	Lignin	Meth-oxyl	Holo-cellu-lose	Cross and Bevan cellulose	Alpha-cellu-lose	Pen-tosans	Acetyl
	Cold water	Hot water	Ether	Alcohol-benzene	1 percent sodium hydroxide								
	Percent												
Pignut													
Sapwood	4.9	6.5	0.3	--	19.1	0.4	21.9	5.6	--	56.1	--	19.3	2.6
Heartwood	2.1	3.0	.4	--	15.1	.5	22.9	5.8	--	56.8	--	18.7	2.2
Shellbark	4.8	5.6	.6	--	19.0	.7	23.4	5.6	--	56.2	--	19.6	1.8
Mockernut	--	3.1	.3	2.3	14.8	--	22.8	--	72.7	--	51.1	18.7	--
Pignut	--	2.0	.2	1.7	13.5	--	25.5	--	73.2	--	50.8	17.8	--
Sand	--	6.7	.4	3.8	18.4	1.0	22.7	--	68.5	--	50.0	16.6	--
Shagbark	--	5.2	.4	3.4	17.6	.6	21.4	--	71.3	--	48.4	18.0	--
Bitter pecan	--	4.6	.5	3.6	16.4	--	25.1	--	--	55.8	44.4	19.2	--

1/ McGovern, J. N., Keller, E. L., and Martin, J. S. Pulps and corrugating paperboards from farm woodland hickory. Forest Products Laboratory Report R1753. 1949.

2/ Ritter, G. J. and Fleck, L. C. Chemistry of wood. V. Results of analysis of some American woods. Indus. and Eng. Chem. 14:1050-1054. 1922

3/ Ritter, G. J. and Fleck, L. C. Chemistry of wood. VI. The results of analysis of heartwood and sapwood of some American woods. Ind. and Eng. Chem. 15:1055-1056. 1923.

4/ Each of subcomponents determined on the original wood.

Table 3.--Tannin content of the bark of several hickory species [1/] [2/]

Species	Tannin content
	Percent
Bitternut	7.8
Mockernut	Insignificant
Shagbark	Do
Pignut	7.6 - 10.0
Sand hickory	6.7
Shellbark	4.7
Pecan	5.7

1/ Russell, A. (with Kaczka, E. A., Tebbens, W. G., Vanneman, C. R. and Cody, Sophia). Natural tanning materials of the Southeastern United States. VI. The trees of the Piedmont section. Jour. Amer. Leather Chemists Assoc. 39:173-178. 1944.

2/ Russell, A. with Vanneman, Clinton R., and Waddey, Walter E. Natural tanning materials of the Southeastern United States. VIII. Mountain species. Jour. Amer. Leather Chemists Assoc. 40:422-426. 1945.

Table 4.--Composition of ash of Georgia woods [1] (percentage of ash based on weight of wood at 10 percent moisture content)

Species	Ash	Potassium oxide	Sodium oxide	Calcium oxide	Magnesium oxide	Phosporus pentoxide	Sulfate	Chloride	Silica	Ferric oxide	Carbon	Carbon dioxide
	Percent											
Mockernut hickory	0.73	18.93	3.38	25.21	6.66	7.98	2.06	0.28	1.80	0.25	1.20	32.44
Red oak	.85	16.41	3.68	32.25	3.58	7.04	2.29	.68	.97	.21	1.38	31.85
White oak	.37	29.90	1.94	21.21	2.43	6.72	4.11	1.00	3.20	.50	3.87	25.16
Shortleaf pine	.35	12.97	1.18	43.31	2.11	2.75	.86	.67	2.35	.18	.74	33.26
Longleaf pine	.49	10.34	2.34	37.24	4.21	2.65	4.32	.21	3.41	2.76	1.11	31.47

1/ Schorger, A. W. The chemistry of cellulose and wood. 596 pp., illus. New York. 1926

Table 5.--Composition of barks [1] (based on weight of ovendry bark)

Species	Ash	Material soluble in successive extractions with: Benzene	Alcohol	Hot water	1 percent sodium hydroxide	Solubility of original bark in 1 percent sodium hydroxide	Apparent "lignin" [2]	Reducing sugar [3] as glucose
	Percent							
Pecan	7.5	0.8	18.4	5.4	25.3	50.9	24.9	30.7
Sweetgum	5.7	1.5	17.7	7.4	21.3	48.3	25.3	33.5
Yellow birch	1.7	4.3	10.8	2.3	28.4	46.9	40.6	31.8
White oak	10.7	2.7	4.4	5.8	26.5	38.2	31.8	28.2
Slash pine	.6	3.4	10.6	3.7	28.9	48.5	49.9	29.8

1/ Chang, Ying-Pe and Mitchell, R. L. Chemical composition of common North American pulpwood barks. Tappi 38:1955. (In press.)

2/ Acid-insoluble product by the 72 percent sulfuric acid method for lignin.

3/ From total hydrolysis by 72 percent sulfuric acid.

Table 6.--Chemical composition of nuts [1] [2]

Kind of nuts	Composition: Shells	Moisture	Protein	Fats	Carbohydrate	Ash	Fuel value [3] per pound
	Percent						Calories
Pecan	50.1	3.4	12.1	70.7	12.2	1.6	3,300
Hickory	62.2	3.7	15.4	67.4	11.4	2.1	3,345
Butternut	86.4	4.5	27.9	61.2	3.4	3.0	3,370
Walnut (black)	74.1	2.5	27.6	56.3	11.7	1.9	3,105
Beech	36.9	6.6	21.8	49.9	18.0	3.7	2,740

1/ Smith, J. Russell. Tree crops. 333 pp., illus. New York. 1929.

2/ Percentage yields based on ovendry edible portion, except for shells, for which yields are based on weight of ovendry shell plus edible portion.

3/ Food value of edible portion.

Table 7.--Composition of nutshells [1] (based on weight of ovendry shell)

Source of shells	Ash	Material soluble in consecutive extractions with:			Pentosans	Crude cellulose	"Lignin" [2]
		Alcohol-benzene	Hot water	1 percent hydrochloric acid			
	Percent						
Pecan	1.5	3.1	7.8	26.2	19.7	26.6	27.3
English walnut	1.6	4.4	8.1	33.1	26.3	34.1	21.0
Coconut	.6	5.8	2.8	29.7	30.1	33.5	35.5

1/ Phillips, M. and Goss, M. J. The composition of certain nutshells. Assoc. of Off. Agric. Chemists 23:662-664. 1942.

2/ Acid-insoluble product by the fuming hydrochloric acid method for lignin.

Table 8.--Nitrogen, calcium, and magnesium content of leaves from various species 1/ (percentage of element on ovendry basis)

Species	Nitrogen	Calcium	Magnesium
	Percent		
Hickory	0.62	2.78	0.62
Yellow-poplar	.53	2.61	.72
Red maple	.51	1.32	.33
American sweetgum	.49	1.30	.47
Shortleaf pine	.45	.59	.19
Loblolly pine	.31	.43	.15

1/ Metz, Louis J. Weight and nitrogen and calcium content of the annual litter fall of forests in the South Carolina Piedmont. Soil Sci. Proc. 16(1): 38-41. 1952.

Table 9.--Yields of distillation products from heartwood of various species 1/

Species	Methyl alcohol	Acetic acid	Charcoal	Tar
	Percent			
Hickory	2.08	5.05	37.7	13.0
Maple	1.94	5.66	40.2	12.5
Birch	1.62	6.19	36.4	12.6
Beech	2.23	5.77	40.6	9.1
White oak	1.34	4.97	49.5	6.3

1/ Wise, L. E. Wood chemistry. 900 pp., illus. New York. 1946.

Table 10.--Yields of potential and fermentable sugar from several American woods 1/

Species	Potential reducing sugar	Fermentable sugar by yeast sorption
	Percent	
Pecan hickory	64.0	40.4
Red oak	63.6	40.0
Yellow-poplar	70.9	53.9
Willow	72.0	54.5
Southern yellow pine	64.8	53.3
Eastern white pine	66.5	58.3
Douglas-fir	66.6	57.4

1/ Saeman, J. F., Bubl, J. L. and Harris, E. E. Quantitative saccharification of wood and cellulose. Indus. and Eng. Chem., Analyt. Ed. 17:35-37. 1945.

HICKORY REPORTS PLANNED

Location and extent of hickories.
Managing hickory in the hardwood stand.
Grading and measuring hickory trees, logs, and products.
Stresses in living hickory and their importance.
The chemistry of hickory. *
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Products obtained from hickory logs.
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The preservative treatment of hickory for other products.
Marketing of hickory.

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